Decoherence control: A feedback mechanism based on hamiltonian tracking

Gil Katz,[1] Mark A. Ratner,[1] and Ronnie Kosloff[2]

[1]*Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113*

[2]*Fritz Haber Research Center for Molecular Dynamics,*

Hebrew University of Jerusalem, Jerusalem, 91904, Israel

(Dated: February 1, 2008)

Abstract

Enviroment - caused dissipation disrupts the hamiltonian evolution of all quantum systems not fully isolated from any bath. We propose and examine a feedback-control scheme to eliminate such dissipation, by tracking the free hamiltonian evolution. We determine a driving-field that maximizes the projection of the actual molecular system onto the freely propagated one. The evolution of a model two level system in a dephasing bath is followed, and the driving field that overcomes the decoherence is calculated. An implementation of the scheme in the laboratory using feedback control is suggested.

PACS number: 82.50.Nd 02.30.Yy 82.53.Kp 33.80.Ps

arXiv:quant-ph/0603021v1   2 Mar 2006

The Schrödinger equation describes time evolution of isolated quantum systems. Any real system, unless very carefully isolated, will decohere due to bath interactions[1, 2, 3, 4, 5, 6, 7, 8, 9, 10].

The approach to decoherence correction taken here derives from tracking control theory. Tracking control originated from the idea of changing the local field in order to follow a reference state [11, 12, 13, 14]. Tracking can be considered as local control with a time dependent target.Since generation of interference pathways is a global process in time, an intervention at one instant influences the subsequent evolution and can interfere at later times with another intervention.

The basic idea here is to use a freely propagating molecule as a tracking target for an identical molecule in a dissipative environment. The perfect tracking field will then null the dissipative forces and protect the molecule from decoherence. The question to be addressed is how can an external field, that generates a unitary transformation, protect the system against non unitary dissipative forces? A computational model of an on-line, dynamic, decoherence control method is explored. The method is established by simultaneously following the evolution in time of a system with and without the bath, thus using the overlap between the two systems to construct a correcting electric field which is directly applied back on the system. The method is explored for the fastest dissipative mechanism, environment-induced electronic quenching from an excited state to a lower state (the approximate decay time in solid state systems is less than 50 fsec). The coherence time of the system is extended by an order of magnitude using the simplest tracking method.

Measuring the overlap between the controlled and the target system also underlies a proposed experimental approach. This observable can then be employed as a basis for a learning loop used to optimize a control field.

The molecular system is described by the density operator $\hat{\boldsymbol{\rho}}$, a function of nuclear and electronic degrees of freedom. The reference or target system $\hat{\boldsymbol{\rho}}_{tar}$, evolves freely under its Hamiltonian $\hat{\mathbf{H}}_0$:

$$\dot{\hat{\rho}}_{tar} = -i[\hat{\mathbf{H}}_0, \hat{\boldsymbol{\rho}}_{tar}] \tag{1}$$

where $\hbar \equiv 1$ is chosen. The subjected system $\hat{\boldsymbol{\rho}}_S$ is coupled to a bath and therefore evolves

according to the dynamics of an open quantum system [15]:

$$\dot{\boldsymbol{\rho}}_S = -i[\hat{\mathbf{H}}_0, \hat{\boldsymbol{\rho}}_S] + \mathcal{L}_D(\hat{\boldsymbol{\rho}}_S) \quad , \tag{2}$$

Here $\mathcal{L}_D$ describes the bath-induced decoherence dynamics, conveniently cast into the Lindblad semigroup form:

$$\mathcal{L}_D(\hat{\boldsymbol{\rho}}_S) = \sum_j \left(\hat{\mathbf{F}}_j \hat{\boldsymbol{\rho}}_S \hat{\mathbf{F}}_j^\dagger - \frac{1}{2}\{\hat{\mathbf{F}}_j \hat{\mathbf{F}}_j^\dagger, \hat{\boldsymbol{\rho}}_S\} \right) \quad , \tag{3}$$

where $\{\hat{\mathbf{A}}, \hat{\mathbf{B}}\} = \hat{\mathbf{A}}\hat{\mathbf{B}} + \hat{\mathbf{B}}\hat{\mathbf{A}}$ is the anti commutator and $\hat{\mathbf{F}}$ are operators from the Hilbert space of the system. The nature of the bath interaction determines the form of the Lindblad operators $\hat{\mathbf{F}}$. The choice of $\hat{\mathbf{F}}$ determines the dissipative model considered.

Our purpose is to control the system coupled to the bath and force it to follow as closely as possible the dynamics of the freely evolving reference system, $\hat{\boldsymbol{\rho}}_{tar}$. The external control field $\epsilon(t)$ is coupled to the system through the transition dipole of the molecule. The control Hamiltonian becomes, $\hat{\mathbf{H}}_c = \hat{\boldsymbol{\mu}}\epsilon(t)$ leading to the dynamics of the controlled system $\hat{\boldsymbol{\rho}}_C$:

$$\dot{\boldsymbol{\rho}}_C = -i[\hat{\mathbf{H}}_0, \hat{\boldsymbol{\rho}}_C] - i[\hat{\mathbf{H}}_c, \hat{\boldsymbol{\rho}}_C] + \mathcal{L}_D(\hat{\boldsymbol{\rho}}_C) \quad . \tag{4}$$

The challenge of decoherence control is to find the field, $\epsilon(t)$, that induces the dynamics of the system $\hat{\boldsymbol{\rho}}_C(t)$ to be as close as possible to $\hat{\boldsymbol{\rho}}_{tar}$. This is attacked by maximizing the overlap functional $J(t)$ between the target and controlled states:

$$J(t) = (\hat{\boldsymbol{\rho}}_C \cdot \hat{\boldsymbol{\rho}}_{tar}) \equiv Tr\{\hat{\boldsymbol{\rho}}_C \, \hat{\boldsymbol{\rho}}_{tar}\} = \langle \hat{\boldsymbol{\rho}}_{tar} \rangle \tag{5}$$

$J(t)$ can be interpreted as the expectation of the target density operator in the controlled state. To achieve this target the control field should increase the expectation of the target operator. The Heisenberg equation of motion for the observable $\langle \hat{\boldsymbol{\rho}}_{tar} \rangle$ generated by the control Hamiltonian becomes:

$$\frac{d}{dt}\langle \hat{\boldsymbol{\rho}}_{tar} \rangle = -i\langle [\hat{\mathbf{H}}_c, \hat{\boldsymbol{\rho}}_{\mathbf{tar}}] \rangle = \tag{6}$$

$$-i\epsilon(t)Tr\{\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{\mathbf{tar}}\hat{\boldsymbol{\rho}}_{\mathbf{C}} - \hat{\boldsymbol{\rho}}_{\mathbf{tar}}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{\mathbf{C}}\} \quad . \tag{7}$$

The control field is constructed by requiring maximal $J(t)$, so that $\frac{d}{dt}\langle \hat{\boldsymbol{\rho}}_{\mathbf{tar}} \rangle \geq \mathbf{0}$ at any instant, leading to:

$$\epsilon(t) = -iK \, Tr\{\hat{\boldsymbol{\rho}}_{\mathbf{C}}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{\mathbf{tar}} - \hat{\boldsymbol{\rho}}_{\mathbf{tar}}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{\mathbf{C}}\}^* \quad , \tag{8}$$

where $K = K(t)$ is a positive envelope function with dimension $\frac{energy}{(dipole)^2}$. From Eq. (8) it is clear that the correcting field $\epsilon(t) = 0$ if $\hat{\boldsymbol{\rho}}_{\mathbf{C}}$ approaches $\hat{\boldsymbol{\rho}}_{\mathbf{tar}}$.

We adopt a molecular model system with two electronic states described by the density operator:

$$\hat{\boldsymbol{\rho}} = \begin{pmatrix} \hat{\boldsymbol{\rho}}_{\mathrm{e}} & \hat{\boldsymbol{\rho}}_{\mathrm{eg}} \\ \hat{\boldsymbol{\rho}}_{\mathrm{ge}} & \hat{\boldsymbol{\rho}}_{\mathrm{g}} \end{pmatrix} , \tag{9}$$

where the indices g and e designate the ground and excited electronic states and the sub matrices are functions of the nuclear coordinates. The Hamiltonian of the system has the form:

$$\hat{\mathbf{H}}_{\mathbf{0}} = \begin{pmatrix} \hat{\mathbf{H}}_{\mathrm{e}} & \hat{\mathbf{V}}_{eg} \\ \hat{\mathbf{V}}_{ge} & \hat{\mathbf{H}}_{\mathrm{g}} \end{pmatrix} , \tag{10}$$

with $\hat{\mathbf{H}}_{\mathrm{g/e}} = \hat{\mathbf{T}} + \hat{\mathbf{V}}_{\mathrm{g/e}}$. $\hat{\mathbf{T}}$ is the kinetic energy operator, $\hat{\mathbf{V}}_{\mathrm{g}}$ and $\hat{\mathbf{V}}_{\mathrm{e}}$ are the potential energy operators on the ground and excited electronic states and $\hat{\mathbf{V}}_{eg}$ is the nonadiabatic coupling potential. The control Hamiltonian is chosen as:

$$\hat{\mathbf{H}}_{\mathrm{c}} = \begin{pmatrix} 0 & -\hat{\boldsymbol{\mu}}^{\dagger}{}_{i}\epsilon(t) \\ -\hat{\boldsymbol{\mu}}\epsilon(t) & 0 \end{pmatrix} , \tag{11}$$

where $\hat{\boldsymbol{\mu}}$ is the coordinate dependent electronic transition dipole element.

The dissipation operator $\hat{\mathbf{F}}_{q}$ is chosen to model fast electronic quenching as $\hat{\mathbf{F}}_{q} = \sqrt{\gamma_q}(|e\rangle\langle g|)$. This choice of dissipative term will lead to a process with a characteristic quenching rate γ :

$$\mathcal{L}_{D}(\hat{\boldsymbol{\rho}}) = \gamma \begin{pmatrix} -\hat{\boldsymbol{\rho}}_{e} & -\hat{\boldsymbol{\rho}}_{ge}{}^{\dagger}/2 \\ -\hat{\boldsymbol{\rho}}_{eg}/2 & \hat{\boldsymbol{\rho}}_{e} \end{pmatrix} . \tag{12}$$

The control field form Eq. (8) becomes:

$$\begin{aligned} \epsilon(t) = \ & KIm \left(Tr_Q\{\hat{\boldsymbol{\rho}}_c^{ge}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{tar}^{g}\} + Tr_Q\{\hat{\boldsymbol{\rho}}_c^{e}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{tar}^{ge}\} \right. \\ & -Tr_Q\{\hat{\boldsymbol{\rho}}_{tar}^{ge}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{c}^{g}\} - Tr_Q\{\hat{\boldsymbol{\rho}}_{tar}^{e}\hat{\boldsymbol{\mu}}\boldsymbol{\rho}_{\mathbf{c}}^{\hat{\mathbf{ge}}}\} \\ & -Tr_Q\{\hat{\boldsymbol{\rho}}_{tar}^{g}\hat{\boldsymbol{\mu}}\boldsymbol{\rho}_{\mathbf{c}}^{\hat{\mathbf{eg}}}\} + Tr_Q\{\boldsymbol{\rho}_{\mathbf{c}}^{\hat{\mathbf{g}}}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{tar}^{eg}\} \\ & -Tr_Q\{\boldsymbol{\rho}_{\mathbf{tar}}^{\hat{\mathbf{eg}}}\hat{\boldsymbol{\mu}}\boldsymbol{\rho}_{\mathbf{c}}^{\hat{\mathbf{ge}}}\} + \left. Tr_Q\{\boldsymbol{\rho}_{\mathbf{c}}^{\hat{\mathbf{eg}}}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{tar}^{e}\} \right) \end{aligned} , \tag{13}$$

where Tr_Q is a partial trace over the coordinates.

The computational model is constructed from two electronic states of a diatomic molecule represented by two diabatic potential energy surfaces that are approximated by quadratic
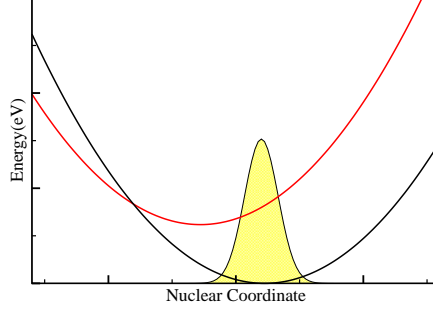
4

FIG. 1: The potential energy surface of the molecular model and the ground initial state. The parameters describing the model are: $\omega_g = \omega_e = 0.07\ eV$, $\Delta = .7\ eV$, $V_{\text{ge/eg}} = 0.05\ eV$, $Q_g = 0$, $Q_e = -0.1$ and $\hat{\mu} = 1.0$.

functions with linear interstate couplings [16]. Using dimensionless normal coordinates:

$$
\begin{aligned}
V_g(\hat{\mathbf{Q}}) &= -\Delta + \tfrac{\omega_g^2}{2}(\hat{\mathbf{Q}} - Q_g)^2 \,, \\
V_e(\hat{\mathbf{Q}}_0) &= \Delta + \tfrac{\omega_e^2}{2}(\hat{\mathbf{Q}} - Q_e)^2 \,,
\end{aligned}
\tag{14}
$$

where ω_g and ω_e are the vibrational frequencies of the ground and excited electronic states, 2Δ is the adiabatic excitation energy. Q_e and Q_g are the equilibrium bond lengths of the two electronic states.

The time evolution was obtained by solving the time dependent Liouville-von Neumann equation. A grid was used for the spatial coordinates and time propagation used the Cheby-chev scheme [17]. The initial ground vibronic state of the system was calculated via a relaxation scheme [18]. A pump pulse transfers a significant fraction of the population from the ground to the excited electronic state. A Gaussian form is chosen for this pulse:

$$
\epsilon_{\text{pump}}(t) = \epsilon_0 e^{-(t-t_{max})^2/2\sigma_L^2} e^{i\omega_L t} \,,
\tag{15}
$$

The carrier frequency ω_L is chosen to match the difference between the ground and excited electronic potentials at the minimum of the ground state $Q = 0$. The width of the pulse σ_L was adjusted to a FWHM duration of 12 fsec and the amplitude $\epsilon_0 \cdot \mu = 0.228 eV$.

At this point three parallel propagations of the density operator were performed. The first for $\hat{\boldsymbol{\rho}}_{tar}$ was carried out only with the Hamiltonian term Eq. (1). The system density operator $\hat{\boldsymbol{\rho}}_S$, was propagated with the dissipative $\mathcal{L}_D$ included, Eq. (2). The controlled density operator, $\hat{\boldsymbol{\rho}}_C$ was propagated with both the dissipative $\mathcal{L}_D$ and the correcting field applied terms, Eq. (4). The correction field was calculated according to Eq. (13) at each time step and fed back in the next time step.
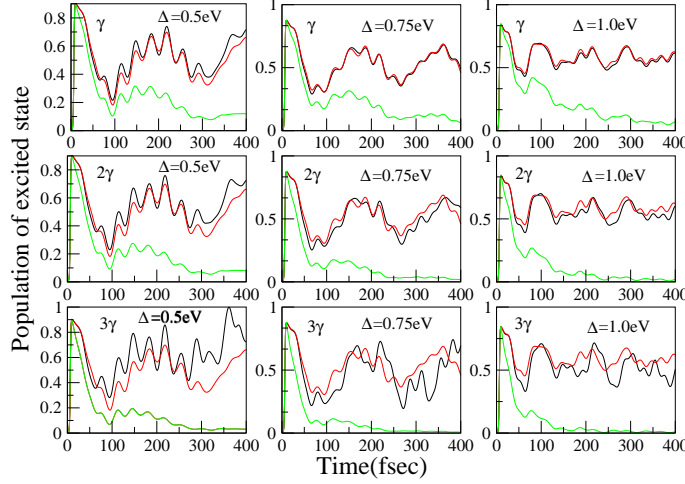
5

FIG. 2: The population of the excited state as a function of time for the target state $\hat{\rho}_{tar}$ (red), the controlled density operator $\hat{\rho}_C$ (black) and the uncontrolled system density operator $\hat{\rho}_S$ (green) for different magnitudes of quenching(columns) and Δ's(rows). $\gamma = 0.003 fsec^{-1}$.

The correction scheme was tested for the the system shown in Fig. 1. The free dynamics represents a complex population oscillation between the two electronic states. The excited state population is shown in Fig. 2 for the controlled $\hat{\rho}_c$, uncontrolled $\hat{\rho}_S$ and target $\hat{\rho}_{tar}$ for different quenching parameters γ and energy gap Δ. In all cases a fast decay of the excited state is seen for the uncontrolled state. The controlled state is able to track the target state and maintain the population. When the quenching increases the controlled system is still able to follow the overall dynamics of the target but not the finer details. As can be seen in Fig. 2, the control ability increases with the energy gap Δ. The control field ϵ is shown in Fig. 3 in time and frequency. In general the field is composed of a central frequency corrosponding to the energy gap modulated by the vibrational frequency. The actual vibronic lines are missing from the spectrum [19]. Wigner plots (not shown) show phase locking between the frequency components.

The changes in purity $Tr\{\hat{\rho}^2\}$ and in the scalar product with the target state $(\hat{\rho} \cdot \hat{\rho}_{tar})$, show a different viewpoint on the decoherence control Fig. 4. The uncontrolled state $\hat{\rho}_S$ undergoes fast exponential decay of both measures in time. The controlled purity $Tr\{\hat{\rho}_C^2\}$ maintains a high value as does as the scalar product $(\hat{\rho}_C \cdot \hat{\rho}_{tar})$ The general trend is a linear decay in time. The oscillations around this decay and the temporal increase in purity suggest that a cooling mechanism is taking place [19]. To gain insight on this possibility
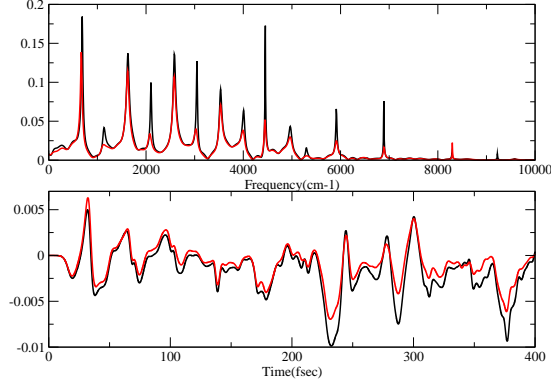
6

FIG. 3: Typical control field in frequency (top left) and time domain (bottom) for $\gamma = 0.003$(red) and $\gamma = 0.006 \ \ fsec^{-1}$(blue).

the correcting field was stopped for 100 fsec and resumed again, Fig. 5. As expected, once the control field is turned off the purity and the scalar product of the controlled state $\hat{\boldsymbol{\rho}}_C$ decease sharply. When the controlling field is resumed an almost linear increase in both parameters can be observed. Such an effect can only be a result of a cooling mechanism which represents an interplay between the nonunitary dissipation and the unitary control field [19]. It is clear [20] that simple unitary transformation cannot induce cooling.

The present results show that the decoherence can be suppressed, extending good overlap with the target by an order of magnitude in time. The model calculation establishes the principle that a correcting external field can be found which protects the system from decoherence. Here we discuss control to overcome fast electronic dephasing; while the rapid modulations in Fig. 3 are not currently attainable, the essential behaviour is correct.

The proof of principle then shifts the attention to finding such a field in the laboratory. The idea is to use an actual freely evolving hamiltonian subsystem as the target for an identical hamiltonian subsystem subject to a dissipative environment such as in solution or on a surface. The correcting feedback should be set such that the difference in transient absorption of the two molecules is minimized.

To implement the present scheme in the laboratory the key element is to apply a scalar product between the states of the reference and controlled systems: $(\hat{\boldsymbol{\rho}}_C \cdot \hat{\boldsymbol{\rho}}_{tar})$ (displayed in Fig.4). To make this task possible the two isolated states should become part of the same quantum system. This can be carried out by placing the controlled system $\hat{\boldsymbol{\rho}}_C$ and the reference system $\hat{\boldsymbol{\rho}}_{tar}$ in two branches of an interferometer. A pair of twin ultrashort
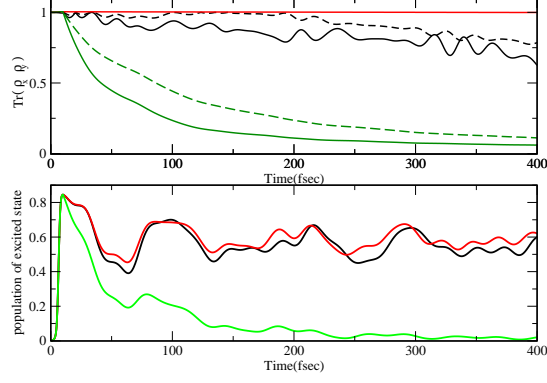
FIG. 4: Top - The purity $Tr\{\hat{\boldsymbol{\rho}}^2\}$ (solid) and the scalar product with the target state $(\hat{\boldsymbol{\rho}} \cdot \hat{\boldsymbol{\rho}}_{tar})$ (dashed) for the target state $\hat{\boldsymbol{\rho}}_C$ (red) the controlled density operator $\hat{\boldsymbol{\rho}}_C$ (black) and the reference uncontrolled density operator $\hat{\boldsymbol{\rho}}_S$ (green). Bottom - The population of the excited state, same color codes.
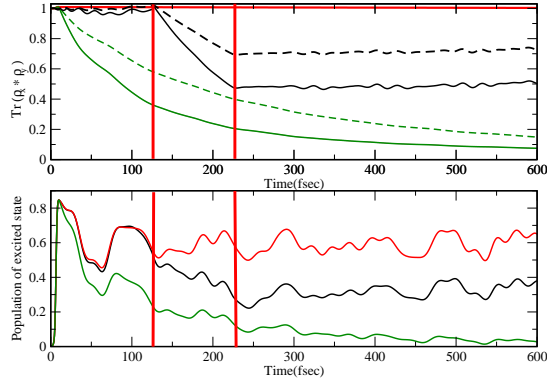

FIG. 5: Turning off the control field. Top -The purity $Tr\{\hat{\boldsymbol{\rho}}^2\}$ (solid) and the scalar product with the target state $(\hat{\boldsymbol{\rho}} \cdot \hat{\boldsymbol{\rho}}_{tar})$ (dashed) for the target state $\hat{\boldsymbol{\rho}}_{tar}$ (red) the controlled density operator $\hat{\boldsymbol{\rho}}_C$ (black) and the reference uncontrolled density operator $\hat{\boldsymbol{\rho}}_S$ (green). The vertical lines indicate the time interval where the control field is turned off. Bottom - The population of the excited state as a function of time, same color codes.

photons which can be created by down conversion are split spatially. Then they are directed to the two branches of the interferometer interrogating the two systems. The transmitted photons are then redirected to interfere with each other. Any difference between the target and the controlled system will degrade this interference. The interference signal can then be used as a feedback to generate the correcting field [21].

---

[1] E. Fraval, M. Sellars, and j.j. Longdell, Phys. Rev. Lett. **95**, 030506 (2005).

[2] Y. Jing and S. Mukamel, J. Chem. Phys. **89**, 5160 (1988).

[3] S. Mukamel, S. Tretiak, T. Wagerstreiter, and V. Chernyak, J. Chem. Phys. **89**, 5160 (1988).

[4] D. Kohen, C. C. Marston, and D. Tannor, J. Chem. Phys. **107**, 5236 (1997).

[5] D. Kohen and D. J. Tannor, J. Chem. Phys. **107**, 5141 (1997).

[6] E. Bittner and P. Rossky, J. Chem. Phys. **103**, 8130 (1995).

[7] O. Prezhdo and P. Rossky, Phys. Rev. Lett. **81**, 5294 (1998).

[8] Z. P. Karkuszewski, C. Jarzynski, and W. Zurek, Phys. Rev. Lett. **89**, 170405 (2002).

[9] W. Zurek, S. Habib, and J. Paz, Phys. Rev. Lett. **70**, 1187 (1993).

[10] W. Zurek, "PHYSICS TODAY" **44**, 36 (1991).

[11] W. Zhu and M. Smit and H. Rabitz, J. Chem. Phys. **110**, 1905 (1999).

[12] W. Zhu and H. Rabitz, J. Chem. Phys. **119**, 3619 (2003).

[13] M. Guhr and N. Schwentner, Phys. Chem. Chem. Phys **7**, 760 (2005).

[14] M. Guhr, H. Ibrahim, and N. Schwentner, Phys. Chem. Chem. Phys **6**, 5353 (2004).

[15] G. Lindblad, Commun. Math. Phys. **48**, 119 (1976).

[16] H. Köppel, W. Domcke, and L. Cederbaum, Adv. Chem. Phys. **57**, 59 (1984).

[17] W. Huisinga, L. Pesce, R. Kosloff and P. Saalfrank, J. Chem. Phys. **110**, 5538 (1999).

[18] R. Kosloff and H. Tal-Ezer, Chem. Phys. Lett. **127**, 223 (1986).

[19] A. Bartana, R. Kosloff and D. J. Tannor, Chem. Phys. **267**, 195 (2001).

[20] W. Ketterle and D. E. Pritchard, Phys. Rev. A **46**, 4051 (1992).

[21] D.A. Steck, K. Jacobs, H. Mabuchi, T. Bhattacharya and S. Habib, Phys. Rev. Lett. **92**, 223004 (2004).

Decoherence control: A feedback mechanism based on hamiltonian tracking

Gil Katz,[1] Mark A. Ratner,[1] and Ronnie Kosloff[2]

[1]*Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113*

[2]*Fritz Haber Research Center for Molecular Dynamics,*

Hebrew University of Jerusalem, Jerusalem, 91904, Israel

(Dated: March 2, 2006)

Abstract

Enviroment - caused dissipation disrupts the hamiltonian evolution of all quantum systems not fully isolated from any bath. We propose and examine a feedback-control scheme to eliminate such dissipation, by tracking the free hamiltonian evolution. We determine a driving-field that maximizes the projection of the actual molecular system onto the freely propagated one. The evolution of a model two level system in a dephasing bath is followed, and the driving field that overcomes the decoherence is calculated. An implementation of the scheme in the laboratory using feedback control is suggested.

PACS number: 82.50.Nd 02.30.Yy 82.53.Kp 33.80.Ps

The Schrödinger equation describes time evolution of isolated quantum systems. Any real system, unless very carefully isolated, will decohere due to bath interactions[1–10].

The approach to decoherence correction taken here derives from tracking control theory. Tracking control originated from the idea of changing the local field in order to follow a reference state [11–14]. Tracking can be considered as local control with a time dependent target.Since generation of interference pathways is a global process in time, an intervention at one instant influences the subsequent evolution and can interfere at later times with another intervention.

The basic idea here is to use a freely propagating molecule as a tracking target for an identical molecule in a dissipative environment. The perfect tracking field will then null the dissipative forces and protect the molecule from decoherence. The question to be addressed is how can an external field, that generates a unitary transformation, protect the system against non unitary dissipative forces? A computational model of an on-line, dynamic, decoherence control method is explored. The method is established by simultaneously following the evolution in time of a system with and without the bath, thus using the overlap between the two systems to construct a correcting electric field which is directly applied back on the system. The method is explored for the fastest dissipative mechanism, environment-induced electronic quenching from an excited state to a lower state (the approximate decay time in solid state systems is less than 50 fsec). The coherence time of the system is extended by an order of magnitude using the simplest tracking method.

Measuring the overlap between the controlled and the target system also underlies a proposed experimental approach. This observable can then be employed as a basis for a learning loop used to optimize a control field.

The molecular system is described by the density operator $\hat{\boldsymbol{\rho}}$, a function of nuclear and electronic degrees of freedom. The reference or target system $\hat{\boldsymbol{\rho}}_{tar}$, evolves freely under its Hamiltonian $\hat{\mathbf{H}}_0$:

$$\dot{\hat{\boldsymbol{\rho}}}_{tar} \quad = \quad -i[\hat{\mathbf{H}}_0, \hat{\boldsymbol{\rho}}_{tar}] \quad , \tag{1}$$

where $\hbar \equiv 1$ is chosen. The subjected system $\hat{\boldsymbol{\rho}}_S$ is coupled to a bath and therefore evolves according to the dynamics of an open quantum system [15]:

$$\dot{\hat{\boldsymbol{\rho}}}_S = -i[\hat{\mathbf{H}}_0, \hat{\boldsymbol{\rho}}_S] + \mathcal{L}_D(\hat{\boldsymbol{\rho}}_S) \quad , \tag{2}$$

Here $\mathcal{L}_D$ describes the bath-induced decoherence dynamics, conveniently cast into the Lindblad semigroup form:

$$\mathcal{L}_{\mathrm{D}}(\hat{\boldsymbol{\rho}}_{\mathrm{S}}) = \sum_j \left(\hat{\mathbf{F}}_j \hat{\boldsymbol{\rho}}_{\mathrm{S}} \hat{\mathbf{F}}_j^\dagger - \frac{1}{2}\{\hat{\mathbf{F}}_j \hat{\mathbf{F}}_j^\dagger, \hat{\boldsymbol{\rho}}_{\mathrm{S}}\} \right) \quad , \tag{3}$$

where $\{\hat{\mathbf{A}}, \hat{\mathbf{B}}\} = \hat{\mathbf{A}}\hat{\mathbf{B}} + \hat{\mathbf{B}}\hat{\mathbf{A}}$ is the anti commutator and $\hat{\mathbf{F}}$ are operators from the Hilbert space of the system. The nature of the bath interaction determines the form of the Lindblad operators $\hat{\mathbf{F}}$. The choice of $\hat{\mathbf{F}}$ determines the dissipative model considered.

Our purpose is to control the system coupled to the bath and force it to follow as closely as possible the dynamics of the freely evolving reference system, $\hat{\boldsymbol{\rho}}_{tar}$. The external control field $\epsilon(t)$ is coupled to the system through the transition dipole of the molecule. The control Hamiltonian becomes, $\hat{\mathbf{H}}_c = \hat{\boldsymbol{\mu}}\epsilon(t)$ leading to the dynamics of the controlled system $\hat{\boldsymbol{\rho}}_C$:

$$\dot{\hat{\boldsymbol{\rho}}}_C = -i[\hat{\mathbf{H}}_0, \hat{\boldsymbol{\rho}}_C] - i[\hat{\mathbf{H}}_c, \hat{\boldsymbol{\rho}}_C] + \mathcal{L}_D(\hat{\boldsymbol{\rho}}_C) \quad . \tag{4}$$

The challenge of decoherence control is to find the field, $\epsilon(t)$, that induces the dynamics of the system $\hat{\boldsymbol{\rho}}_C(t)$ to be as close as possible to $\hat{\boldsymbol{\rho}}_{tar}$. This is attacked by maximizing the overlap functional $J(t)$ between the target and controlled states:

$$J(t) = (\hat{\boldsymbol{\rho}}_C \cdot \hat{\boldsymbol{\rho}}_{tar}) \equiv Tr\{\hat{\boldsymbol{\rho}}_C \ \hat{\boldsymbol{\rho}}_{tar}\} = \langle \hat{\boldsymbol{\rho}}_{tar} \rangle \tag{5}$$

$J(t)$ can be interpreted as the expectation of the target density operator in the controlled state. To achieve this target the control field should increase the expectation of the target operator. The Heisenberg equation of motion for the observable $\langle \hat{\boldsymbol{\rho}}_{tar} \rangle$ generated by the control Hamiltonian becomes:

$$\frac{d}{dt}\langle \hat{\boldsymbol{\rho}}_{tar} \rangle = -i\langle [\hat{\mathbf{H}}_c, \hat{\boldsymbol{\rho}}_{\mathbf{tar}}] \rangle = \tag{6}$$

$$-i\epsilon(t)Tr\{\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{\mathbf{tar}}\hat{\boldsymbol{\rho}}_{\mathbf{C}} - \hat{\boldsymbol{\rho}}_{\mathbf{tar}}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{\mathbf{C}}\} \quad . \tag{7}$$

The control field is constructed by requiring maximal $J(t)$, so that $\frac{d}{dt}\langle \hat{\boldsymbol{\rho}}_{\mathbf{tar}} \rangle \geq \mathbf{0}$ at any instant, leading to:

$$\epsilon(t) = -iK \ Tr\{\hat{\boldsymbol{\rho}}_{\mathbf{C}}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{\mathbf{tar}} - \hat{\boldsymbol{\rho}}_{\mathbf{tar}}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{\mathbf{C}}\}^* \quad , \tag{8}$$

where $K = K(t)$ is a positive envelope function with dimension $\frac{energy}{(dipole)^2}$. From Eq. (8) it is clear that the correcting field $\epsilon(t) = 0$ if $\hat{\boldsymbol{\rho}}_{\mathbf{C}}$ approaches $\hat{\boldsymbol{\rho}}_{\mathbf{tar}}$.

We adopt a molecular model system with two electronic states described by the density operator:

$$\hat{\rho} \;=\; \begin{pmatrix} \hat{\rho}_e & \hat{\rho}_{eg} \\ \hat{\rho}_{ge} & \hat{\rho}_g \end{pmatrix} \;, \tag{9}$$

where the indices g and e designate the ground and excited electronic states and the sub matrices are functions of the nuclear coordinates. The Hamiltonian of the system has the form:

$$\hat{\mathbf{H}}_0 = \begin{pmatrix} \hat{\mathbf{H}}_e & \hat{\mathbf{V}}_{eg} \\ \hat{\mathbf{V}}_{ge} & \hat{\mathbf{H}}_g \end{pmatrix} \;, \tag{10}$$

with $\hat{\mathbf{H}}_{g/e} = \hat{\mathbf{T}} + \hat{\mathbf{V}}_{g/e}$. $\hat{\mathbf{T}}$ is the kinetic energy operator, $\hat{\mathbf{V}}_g$ and $\hat{\mathbf{V}}_e$ are the potential energy operators on the ground and excited electronic states and $\hat{\mathbf{V}}_{eg}$ is the nonadiabatic coupling potential. The control Hamiltonian is chosen as:

$$\hat{\mathbf{H}}_c = \begin{pmatrix} 0 & -\hat{\boldsymbol{\mu}}^{\dagger}{}_i\epsilon(t) \\ -\hat{\boldsymbol{\mu}}\epsilon(t) & 0 \end{pmatrix} \;, \tag{11}$$

where $\hat{\boldsymbol{\mu}}$ is the coordinate dependent electronic transition dipole element.

The dissipation operator $\hat{\mathbf{F}}_q$ is chosen to model fast electronic quenching as $\hat{\mathbf{F}}_q = \sqrt{\gamma_q}(|e\rangle\langle g|)$. This choice of dissipative term will lead to a process with a characteristic quenching rate γ :

$$\mathcal{L}_D(\hat{\boldsymbol{\rho}}) \;=\; \gamma \begin{pmatrix} -\hat{\boldsymbol{\rho}}_e & -\hat{\boldsymbol{\rho}}_{ge}{}^{\dagger}/2 \\ -\hat{\boldsymbol{\rho}}_{eg}/2 & \hat{\boldsymbol{\rho}}_e \end{pmatrix} \;. \tag{12}$$

The control field form Eq. (8) becomes:

$$\begin{aligned} \epsilon(t) \;=\; & KIm\,(\; Tr_Q\{\hat{\boldsymbol{\rho}}_c^{ge}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{tar}^g\} + Tr_Q\{\hat{\boldsymbol{\rho}}_c^e\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{tar}^{ge}\} \\ & -Tr_Q\{\hat{\boldsymbol{\rho}}_{tar}^{ge}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_c^g\} - Tr_Q\{\hat{\boldsymbol{\rho}}_{tar}^e\hat{\boldsymbol{\mu}}\boldsymbol{\rho}_c^{\hat{\mathbf{ge}}}\} \\ & -Tr_Q\{\hat{\boldsymbol{\rho}}_{tar}^g\hat{\boldsymbol{\mu}}\boldsymbol{\rho}_c^{\hat{\mathbf{eg}}}\} + Tr_Q\{\boldsymbol{\rho}_c^{\hat{\mathbf{g}}}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{tar}^{eg}\} \\ & -Tr_Q\{\boldsymbol{\rho}_{\mathbf{tar}}^{\hat{\mathbf{eg}}}\hat{\boldsymbol{\mu}}\boldsymbol{\rho}_c^{\hat{\mathbf{ge}}}\} + Tr_Q\{\boldsymbol{\rho}_c^{\hat{\mathbf{eg}}}\hat{\boldsymbol{\mu}}\hat{\boldsymbol{\rho}}_{tar}^e\} \;) \end{aligned} \tag{13}$$

where Tr_Q is a partial trace over the coordinates.

The computational model is constructed from two electronic states of a diatomic molecule represented by two diabatic potential energy surfaces that are approximated by quadratic
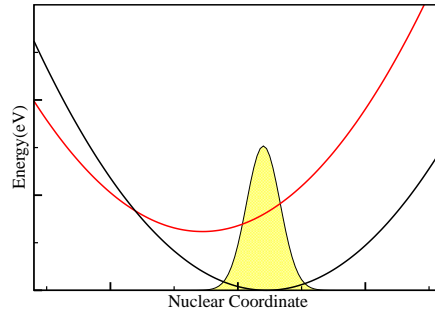
FIG. 1: The potential energy surface of the molecular model and the ground initial state. The parameters describe the model are: $\omega_g = \omega_e = 0.07 \ eV$, $\Delta = .7 \ eV$,$V_{\mathrm{ge/eg}} = 0.05 \ eV$, $Q_g = 0$, $Q_e = -0.1$ and $\hat{\mu} = 1.0$.

functions with linear interstate couplings [16]. Using dimensionless normal coordinates:

$$
\begin{aligned}
V_g(\hat{\mathbf{Q}}) &= -\Delta + \frac{\omega_g^2}{2}(\hat{\mathbf{Q}} - Q_g)^2 \ , \\
V_e(\hat{\mathbf{Q}}_0) &= \Delta + \frac{\omega_e^2}{2}(\hat{\mathbf{Q}} - Q_e)^2 \ ,
\end{aligned}
\tag{14}
$$

where ω_g and ω_e are the vibrational frequencies of the ground and excited electronic states, 2Δ is the adiabatic excitation energy. Q_e and Q_g are the equilibrium bond lengths of the two electronic states.

The time evolution was obtained by solving the time dependent Liouville-von Neumann equation. A grid was used for the spatial coordinates and time propagation used the Cheby-chev scheme [17]. The initial ground vibronic state of the system was calculated via a relaxation scheme [18]. A pump pulse transfers a significant fraction of the population from the ground to the excited electronic state. A Gaussian form is chosen for this pulse:

$$
\epsilon_{\mathrm{pump}}(t) = \epsilon_0 \mathrm{e}^{-(t - t_{max})^2 / 2\sigma_L^2} \mathrm{e}^{i\omega_L t} \ ,
\tag{15}
$$

The carrier frequency ω_L is chosen to match the difference between the ground and excited electronic potentials at the minimum of the ground state $Q = 0$. The width of the pulse σ_L was adjusted to a FWHM duration of 12 fsec and the amplitude $\epsilon_0 \cdot \mu = 0.228 eV$.

At this point three parallel propagations of the density operator were performed. The first for $\hat{\rho}_{tar}$ was carried out only with the Hamiltonian term Eq. (1). The system density operator $\hat{\rho}_S$, was propagated with the dissipative $\mathcal{L}_D$ included, Eq. (2). The controlled density operator, $\hat{\rho}_C$ was propagated with both the dissipative $\mathcal{L}_D$ and the correcting field applied terms, Eq. (4). The correction field was calculated according to Eq. (13) at each time step and fed back in the next time step.
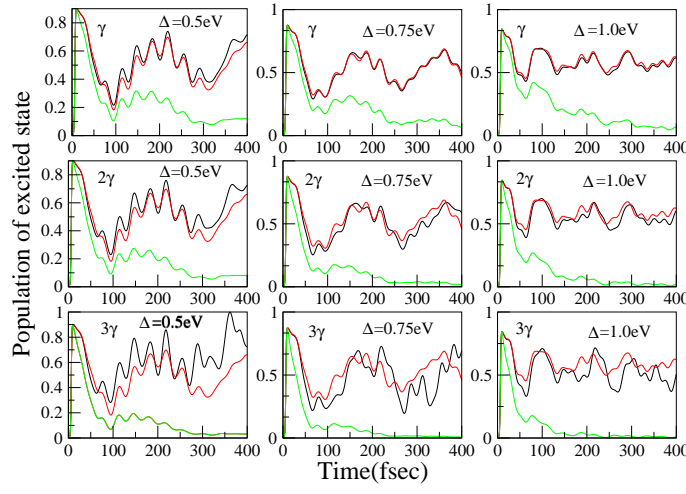
FIG. 2: The population of the excited state as a function of time for the target state $\hat{\boldsymbol{\rho}}_{tar}$ (red), the controlled density operator $\hat{\boldsymbol{\rho}}_C$ (black) and the uncontrolled system density operator $\hat{\boldsymbol{\rho}}_S$ (green) for different magnitudes of quenching(columns) and Δ's(rows). $\gamma = 0.003 fsec^{-1}$.

The correction scheme was tested for the the system shown in Fig. 1. The free dynamics represents a complex population oscillation between the two electronic states. The excited state population is shown in Fig. 2 for the controlled $\hat{\boldsymbol{\rho}}_c$, uncontrolled $\hat{\boldsymbol{\rho}}_S$ and target $\hat{\boldsymbol{\rho}}_{tar}$ for different quenching parameters γ and energy gap Δ. In all cases a fast decay of the excited state is seen for the uncontrolled state. The controlled state is able to track the target state and maintain the population. When the quenching increases the controlled system is still able to follow the overall dynamics of the target but not the finer details. As can be seen in Fig. 2, the control ability increases with the energy gap Δ. The control field ϵ is shown in Fig. 3 in time and frequency. In general the field is composed of a central frequency corrosponding to the energy gap modulated by the vibrational frequency. The actual vibronic lines are missing from the spectrum [19]. Wigner plots (not shown) show phase locking between the frequency components.

The changes in purity $Tr\{\hat{\boldsymbol{\rho}}^2\}$ and in the scalar product with the target state $(\hat{\boldsymbol{\rho}} \cdot \hat{\boldsymbol{\rho}}_{tar})$, show a different viewpoint on the decoherence control Fig. 4. The uncontrolled state $\hat{\boldsymbol{\rho}}_S$ undergoes fast exponential decay of both measures in time. The controlled purity $Tr\{\hat{\boldsymbol{\rho}}_C^2\}$ maintains a high value as does as the scalar product $(\hat{\boldsymbol{\rho}}_C \cdot \hat{\boldsymbol{\rho}}_{tar})$ The general trend is a linear decay in time. The oscillations around this decay and the temporal increase in purity suggest that a cooling mechanism is taking place [19]. To gain insight on this possibility

6